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TECHNICAL/ECONOMIC SURVEY OF THE MARKETABILITY OF U.S. ARMY PHO--ETC(U)
MAY 78 M E HILLMAN, E W HELPER, W GORDON

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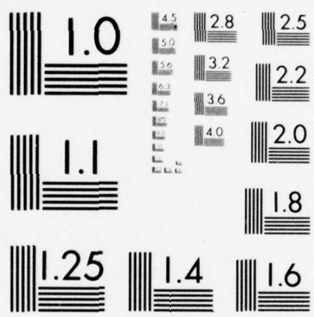

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Carbonyl Chloride	Monoiscyanates	106A500X containers
Diisocyanates	Pesticides	
TDT	Pharmacenticals	
MDI	Gas distributors	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A survey of over 40 industrial companies to determine feasibility and best approach for sale of surplus DOD low-grade phosgene. Fourteen companies expressed an interest in the phosgene and/or associated ton containers. Summary data includes production and capacity of facilities for consumption of phosgene and related end products, quality of phosgene required, and an estimate of suitable marketing approach. Containers included with the phosgene consisted of 428 one-ton cylinder and 367 106A500X containers.

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FINAL REPORT

on

TECHNICAL/ECONOMIC SURVEY OF
THE MARKETABILITY OF U.S. ARMY
PHOSGENE (CARBONYL CHLORIDE)

to

OFFICE OF THE PROJECT MANAGER FOR CHEMICAL
DEMILITARIZATION AND INSTALLATION RESTORATION
(OPM CDIR), ABERDEEN PROVING GROUND, MARYLAND

May 17, 1978

by

M.E.D HILLMAN, E. W. HELPER,
and W. GORDON

BATTELLE
Columbus Division
505 King Avenue
Columbus, Ohio 43201

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EXECUTIVE SUMMARY

The cost of buying, installing and operating the necessary equipment to redistill approximately 2 million pounds of surplus Army phosgene would probably be prohibitive. Most industrial contacts who would comment on this topic indicated that the cost of redistillation would probably greatly exceed the cost of decontamination (neutralization). This indicates that surplus Army phosgene should be used for those reactions that do not require high purity phosgene. Some products that can be made with low grade phosgene are:

- Carbonates
- Chloroformates
- Chlorothioformates
- Carbamoyl chlorides
- Pesticides

Materials that require high purity (>99 percent) phosgene in their manufacture are:

- Diisocyanates (TDI, MDI, etc.)
- Polycarbonates
- Peroxycarbonates
- Pharmaceuticals

Manufacturers of these latter materials generally have no interest in low-grade surplus Army phosgene.

During the course of this investigation, BCD identified 14 companies that have some interest in purchasing surplus Army phosgene. These companies are identified in the Battelle report. All of these companies would like to be notified by the Army of any future bidding announcements. One strategy that might be employed to expedite the removal of the phosgene from RMA, is to make the phosgene available to any company on basically the same contractual basis as the successful Arapahoe bid. The Army could then select the "winning bidder or bidders" according to the most acceptable removal schedule.

DRAFT REPORT

on

TECHNICAL/ECONOMIC SURVEY OF THE MARKETABILITY OF U.S. ARMY PHOSGENE (CARBONYL CHLORIDE)

to

OFFICE OF THE PROJECT MANAGER FOR CHEMICAL DEMILITARIZATION AND INSTALLATION RESTORATION (OPM CDIR), ABERDEEN PROVING GROUND, MARYLAND

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BATTELLE
Columbus Division

May 17, 1978

INTRODUCTION

Phosgene was originally purchased by the Army as a chemical warfare agent. In the early 1960's, this chemical was declared obsolete. About 5.7 million pounds of phosgene was sold from Rocky Mountain Arsenal (RMA) to two purchasers before shipments were suspended in 1969. On March 30, 1976 legislation PL 94-251 permitted disposition of the remaining phosgene by sales. Approximately 1.8 to 2.0 million pounds of phosgene with containers is available for sale.

Because OPM CDIR does not have the available necessary in-house capability to perform the tasks required, Battelle was requested to do this project.

Objectives

The overall objective of this study is to collect and analyze data about the potential marketability of Army phosgene. The information obtained will be used to determine the best approach for the sale of the existing Army inventory of low-grade phosgene.

To provide the Army with the information necessary to determine the feasibility and best approach for sale of the existing Army inventory of low-grade phosgene, the following data was collected.

(1) Production/capcaity

- U.S. manufacturers
  - production and/or capacities
  - quantities for sale versus captive use
- End products
  - quantities used for each

(2) Quality

- Determine quality required for each end product/process
- Outline purification schemes for each quality level required
- Evaluation of the feasibility of direct use of the low-grade phosgene in the various uses

(3) Marketability

- Make preliminary estimates of the most suitable marketing approach based on:
  - sale on an FOB-origin versus destination basis
  - purification (if needed) at RMA versus contractors site.

Scope

The scope of this project includes the possible sale in the United States of approximately 1.8 million pounds of phosgene. The study also includes the possible sale of the following one ton storage and shipping containers (DOT 106A500X).

Storage containers	Shipping containers (with gas tight bonnet)
850 full at RMA	307 full at RMA
368 empty at RMA	12 empty at RMA
Total 1218	48 full at Arapahoe Chemicals
	Total 367

PRINCIPAL FINDINGS

Over 80 contacts were made to knowledgeable individuals at 40 industrial companies. Fourteen companies (Table 1) expressed an interest in either the phosgene, the cylinders or both. Several of these companies are very eager to obtain the surplus Army phosgene and/or cylinders as soon as possible. A list of all companies contacted is included in Appendix A.

Companies Contacted

The companies contacted were manufacturing companies that produced one or more of the following products.

Product	Percentage of U.S. Phosgene utilized
• Phosgene	-
• Diisocyanates (TDT & MDI)	89
• Polycarbonates	5
• Monoisocyanates	
• Other chemical intermediates	6
• Pesticides	
• Pharmaceuticals	
• Gas manufacturers and distributors	

Phosgene Manufacturers

Because the 1.8 million pounds of surplus Army phosgene represents only about 1/10 of one percent of the U.S. annual phosgene capacity, the large manufacturers cannot efficiently use such small amounts. Also in 17 of the 19 U.S. phosgene plants the production is essentially limited to captive use. For these reasons phosgene manufacturers had little interest in either the phosgene or the cylinders.

TABLE 1. COMPANIES INTERESTED IN SURPLUS ARMY PHOSGENE AND/OR CYLINDERS

Company	Degree of Interest	
	Phosgene	Cylinders
Consolidated Chemical	H	H
Chemical Commodities	H	H
Jones Chemical	M	H
Union Carbide-Linde Division	L	H
Manley-Regan	N	H
Delta Chem	L	M
BASF-Wyandotte	M	N
Rubicon	M	N
Minerec	M	N
Olin	M	N
Matheson Gas Products	M	N
Chemetron	L	L
Union Carbide	L	N
Eastman Kodak	L	N

Key: H = High interest

M = moderate interest

L = low interest

N = no interest

Source: Battelle contacts with industry

Diisocyanate Manufacturers

Toluene diisocyanate (TDI) and methylenebis (4-phenyl isocyanate) (MDI) manufacturers require phosgene of very high purity (99 to 99.9 percent) since the final products, TDI and MDI are not purified and any impurities would end up in the product. The cost of purifying 1.8 million pounds of phosgene would be prohibitive according to some contacts and would probably cost more than disposal/decomtamination costs.

Polycarbonate (PC) Manufacturers

PC manufacturers have no interest in surplus Army phosgene for the same reasons as the diisocyanate manufacturers.

Monoisocyanate Manufacturers

Since most monoisocyanates are volatile and a final purification (distillation) is normally carried out, impure phosgene can be utilized since impurities can be removed at this final purification stage.

Other Chemical Derivative and Intermediate Manufacturers

Other chemical derivatives and intermediates such as carbonates, chloroformates, chlorothioformates and carbamoylchlorides are also volatile and can be purified by distillation. Companies that produce these derivatives could probably also use surplus Army phosgene without purification except for filtration. Peroxycarbonates require high purity phosgene because of their propensity to decompose, sometimes violently.

Pesticide Manufacturers

Not all companies that produce phosgene derived pesticides handle phosgene itself since many pesticides can be made from previously mentioned intermediates such as monoisocyanates, chloroformates, chlorothioformates and carbamoyl chlorides. Impurities, such as iron salts, that would arise from using impure phosgene for pesticide manufacture would probably not be a major problem.

Pharmaceutical Manufacturers

All contacts made with companies that produce pharmaceuticals were adamant about not using impure phosgene. The FDA would probably not allow it. The major bad actor is the free chlorine. The Cl_2 could result in chlorinating organic molecules and could result in toxic and/or carcinogenic impurities in the final product. Also carbon tetrachloride (CCl_4) is carcinogenic and would have to be removed completely before the drug could be formulated and sold. For these reasons possible applications in the pharmaceutical industry were not pursued in depth.

Gas Manufacturers and Distributors

Some of the larger gas manufacturers and distributors were contacted to determine if they had interest in either the gas cylinders or the phosgene. Several of these companies expressed definite interest in cylinders or phosgene or both. These companies are included in Table 1.

Quality of Phosgene Required

The quality of phosgene required for each end product application is indicated in Table 2. It should be noted that the polymer, peroxide and pharmaceutical applications require very high purity phosgene and should not be considered further as possible outlets for

surplus impure Army phosgene. It should be noted that equipment for purifying surplus Army phosgene to meet the requirements of these applications would probably require one to two years to purchase and install. Also the capital costs would probably exceed the corresponding costs for decontamination. For these reasons Battelle suggests that other areas that do not require such high purity phosgene be pursued by the Army. These applications are indicated in Table 2 as areas requiring only about 95 percent phosgene purity.

Purification Schemes

Essentially all industrial contacts indicated that prior filtration of the phosgene would be very desirable. This was particularly true with those contacts that have had previous experience with the RMA phosgene. Several of the latter reported that there was "gummy polymeric material" in the phosgene that resulted in blocking feed lines and equipment. One contact said the "first dozen or so" cylinders received from the Army were good but the rest were bad. A good filtration prior to delivery would greatly expedite disposition of this material.

Alternatively, the Army could do a simple vapor transfer of the phosgene from a full cylinder to a clean empty cylinder. This could be done by connecting the two cylinders together then warming up the full cylinder and cooling the empty cylinder. The phosgene would vaporize then recondense in the empty cylinder. This should remove all solids and high boiling contaminants. However, it would not remove the chlorine (the worst contaminant according to most contacts) unless a precut were taken and discarded (decontaminated). The boiling points of phosgene and chlorine are +7.6 and -34.05, respectively. Since chlorine is considerably more volatile than phosgene, it will tend to vaporize first. If the first one or two percent of the vapors were decontaminated most of the chlorine would probably be removed.

TABLE 2. QUALITY REQUIRED FOR PHOSGENE APPLICATIONS

Phosgene Derivatives	Required Purity	Significant Contaminants	Purification Required
TDI/MDI	> 99%	Cl_2, Fe	Redistillation
Polycarbonates	> 99	Cl_2, Fe	Redistillation
Monisocyanates	~ 95	--	Filtration
Carbonates	~ 95	--	Filtration
Chloroformates	~ 95	--	Filtration
Chlorothioformates	~ 95	--	Filtration
Carbamoyl chlorides	~ 95	--	Filtration
Peroxycarbonates	> 99	Fe, Cl_2	Redistillation
Pesticides	~ 95	--	Filtration
Pharmaceuticals	> 99	Cl_2, CCl_4	Redistillation

The cost of redistillation of the phosgene to meet the requirements of polymer, peroxide or pharmaceutical applications would probably not be justified. All correspondents who would comment on this point indicated that the cost of distillation would probably exceed the cost of decontamination. One phosgene manufacturer said that when a below specification batch was produced, it was decontaminated (destroyed). (Note that this comment was made by a representative of a company with existing distillation equipment.) A second contact with this manufacturer indicated that the main reason for discarding bad batches of phosgene was due to plugging of lines when carbon monoxide was added to consume excess chlorine.

In summary the Army might agree to filter the phosgene in the process of transferring it into the shipping containers, if this is practical. It is probably not necessary for the Army to purify the phosgene further. Sufficient markets exist for filtered surplus Army phosgene so that the markets requiring high purity phosgene need not be considered.

Marketability

The potential marketability of surplus Army phosgene appears high enough, at least initially, to consider only an FOB origin basis. Of course, the Army should cooperate in any reasonable way to expedite the transfer, loading and transport of material.

Purification of the phosgene (other than filtration as mentioned previously) by redistillation at RMA should probably not be considered because of the exceedingly high cost. Purification by redistillation, if needed, should primarily be considered at the contractors site at his expense.

A strategy that might be used to expedite the removal of the phosgene from RMA, would be to make the phosgene available to any company on basically the same contractual basis as that contained in the successful

Arapahoe bid. That is the price of the phosgene and cylinders could be the same as the accepted Arapahoe bid, but the Army would be able to select the successful bidder(s) based on his or their removal schedule and cylinder return schedule. It is anticipated that the most acceptable removal schedule would approximate 25 one ton cylinders per week based strictly on the Army's filling capability. Actually the optimum removal schedule is somewhat higher than 25 per week.

Since we understand the Army can fill 25 cylinders per week, the 850 full storage containers could be transferred into shipping containers in 34 weeks. There are also 307 full shipping containers at RMA or a total of 1157 full containers. If all of the containers were removed in 34 weeks. the average removal rate would be 34 containers per week. This, of course, assumes that emptied shipping containers would be returned starting in the second or third week and on a continuing basis thereafter. Thus the optimum removal rate would be 34 containers per week. The Army could accept the bidder that could most closely meet this schedule. It might be necessary to sell phosgene to more than one company, however, this would probably not be as desirable as having a single contractor.

RESEARCH RESULTS

An initial literature search was made to determine the U.S. companies that may have an interest in either the phosgene or the containers. These manufacturing companies were organized according to the following product classifications:

- Phosgene
- Diisocyanates (TDI, MDI)
- Polycarbonates
- Monoisocyanates
- Other chemical intermediates produced from phosgene
- Pesticides produced from phosgene
- Miscellaneous pharmaceuticals that can utilize phosgene
- Gas manufacturers and distributors.

Each of the above classes of companies will be discussed briefly in the following sections of the report.

Manufacturers of Phosgene

There are presently 17 U.S. manufacturers of phosgene and 19 plants. These plants and their capacities are listed in Table 3. Phosgene plant capacities range from about 5 million pounds to about 300 million pounds. Of the 17 manufacturers of phosgene there are only two (Chemetron and Van De Mark) that are well recognized merchant marketers of phosgene. The other 15 companies (17 plants) produce phosgene for captive use. Almost half of the plants (9) are in the Gulf states (Texas, Louisiana, and Alabama), and the rest are east of the Mississippi River. None of these plants is close to RMA.

Chemistry

Phosgene is prepared by passing a mixture of equivalent (molar) amounts of chlorine and carbon monoxide over an activated carbon catalyst bed.

$$Cl_2 + CO \xrightarrow{C} Cl\text{-}CO\text{-}Cl$$

An excess of carbon monoxide is usually used so as to consume completely all of the chlorine. The catalyst bed must be cooled externally, because the reaction is very exothermic. Most of the carbon monoxide available for phosgene manufacture in the United States is produced from natural gas. Trace amounts of unreated methane (CH_4) in the carbon monoxide are chlorinated to produce carbon tetrachloride (CCl_4) as a trace impurity in the phosgene. Traces of moisture in the Army phosgene should have reacted completely with the phosgene according to the equation:

$$ClCOCl + H_2O \longrightarrow 2\ HCl + CO_2$$

This is an irreversible reaction which should have been complete years ago, so the analytical documents that indicate that water is present in the Army phosgene are probably erroneous.

Manufacturers of Diisocyanates (TDI, MDI)

There are ten U.S. manufacturers of TDI (toluene diisocyanate). Seven of the ten TDI producers have phosgene plants that are designed to supply exactly the amount of phosgene required by their TDI plants. Table 1 lists the phosgene capacity and also the phosgene capacity required for TDI, MDI, and polycarbonate plants. When these two numbers are equal, the remainder column in Table 3 is zero. This occurs for 10 of the 19 phosgene plants. That is, 10 of the U.S. phosgene plants are devoted entirely to TDI, MDI, and polycarbonate manufacturing (no surplus phosgene is produced).

It should be noted that 66 percent of U.S. phosgene capacity is specifically dedicated to TDI manufacture and 23 percent to MDI. This leaves only about 11 percent for all other applications.

... (millions of pounds)

Company	Location	Phosgene Capacity	Phosgene Requirements for:[a] TDI	MDI	Polycarbonate	Remainder	Other
Allied	Moundsville, WV	100	100			0	
BASF Wyandotte	Geismar, LA	130	130			9	
Rubicon (Uniroyal + ICI)	Geismar, LA	125	55	70		0	
Chemetron*	LaPorte, TX	67				67	
Dow	Freeport, TX	130	130			0	
DuPont	Deepwater, NJ	135	135			0	
FMC [b]	Baltimore, MD	(6)[b]				(6)	Chloroformates[b]
GE	Mount Vernon, IN	60			60 (Lexan®)	0	
Jefferson (Texaco)[c]	Port Neches, TX	(30)[c]		(30)[c]		0	
Minerec	Baltimore, MD	8				8	Diethyl carbonate and chloroformates
Mobay	New Martinsville, WV	250	130	99	17 (Merlon®)	4	+7 miscellaneous isocyanates
Mobay	Baytown, TX	250	235		15 (Merlon®)	0	
Olin	Ashtabula, OH	50	50			0	
Olin	Lake Charles, LA	120	120			0	
PPG	Barberton, OH	5				5	Specialty carbonates (peroxides)
Stauffer	Cold Creek, AL	25				25	Pesticides
Story [d]	Muskegon, MI	(10)[d]				(10)[d]	8 miscellaneous isocyanates
Union Carbide	Institute, WV	140	72			68	Methyl isocyanate/pesticides
Upjohn	LaPorte, TX	300		225		75	+6 miscellaneous isocyanates
Van De Mark*	Lockport, NY	8				8	
TOTAL		1738	1157	394	92	101	
Percent		100	66	23	5	6	
Phosgene required/lb. of product		1	1.3	0.9	0.42		

* Merchant Marketer

(a) These numbers are the approximate amount of phosgene required for each use based on published figures and/or industrial contacts.

(b) FMC stopped producing phosgene and chloroformates in 1974

(c) Jefferson is no longer producing phosgene or MDI.

(d) Company filed for bankruptcy in 1976. Cordova, the buyer of the plant and technology, is not manufacturing isocyanates and does not plan to do so before 1980.

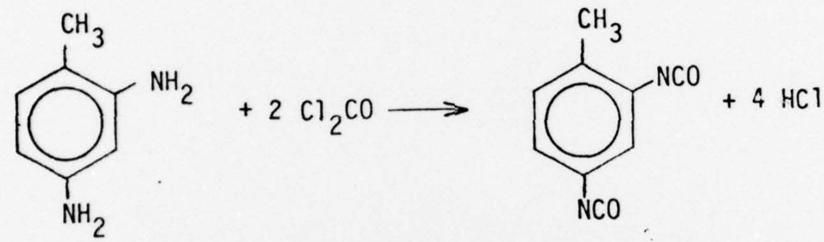
Source: Battelle estimates and calculations.

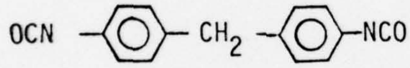
Chemistry

Isocyanates are made by reacting phosgene with a primary amine (RNH_2):

$$RNH_2 + \underset{Cl}{\overset{Cl}{>}}C{=}O \longrightarrow RN{=}C{=}O + 2\ HCl$$

TDI is made from an aromatic diamine according to the equation:



The structure of MDI is: 

Reactions of Isocyanates. Isocyanates are very reactive. Some examples are:

$$RNCO + HOR' \longrightarrow RNH - \overset{\overset{\displaystyle O}{\|}}{C} - OR' \text{ (urethane or carbamate)}$$

$$RNCO + HNR_2' \longrightarrow RNH - \overset{\overset{\displaystyle O}{\|}}{C} - NR_2' \text{ (urea)}$$

$$RNCO + HSR' \longrightarrow RNH - \overset{\overset{\displaystyle O}{\|}}{C} - SR' \text{ (thiocarbamate)}$$

When a diisocyanate such as TDI is reacted with a dihydroxy compound (glycol), both ends of both molecules can react, and high molecular weight polymers (plastics) are produced.

If a controlled amount of water is incorporated in the system, the following reaction also occurs:

$$RNCO + H_2O \longrightarrow RNH_2 + CO_2$$

The CO_2 is a gas and causes the polymerizing mixture to foam as it solidifies. This is the way polyurethane foam cushions for furniture and automobiles are made.

It should be noted that, when diisocyanates are made from diamines, the isocyanate groups can react with amine groups before all of these have been converted to isocyanate groups by the phosgene. For this reason the product actually obtained is an oligomer containing several TDI or MDI precursor molecules bonded together by urea linkages.

$$COCl_2 + H_2N\text{-}R\text{-}NH_2 \longrightarrow OCN\text{-}R\text{-}NH_2 + OCN\text{-}R\text{-}NCO \longrightarrow OCN\text{-}R\text{-}NH\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}NH\text{-}R\text{-}NCO$$

Since the molecule is not a single chemical entity, it cannot be purified by the conventional means of crystallization or distillation. For this reason, the phosgene used to produce diisocyanates must be very pure, and the Army surplus phosgene would not be suitable without extensive and very expensive purification prior to use.

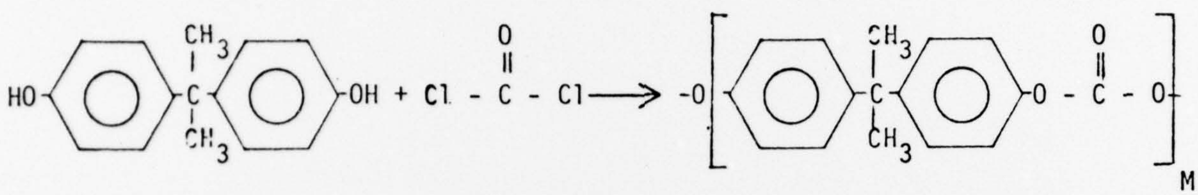
Manufacturers of Polycarbonates

Two U.S. companies (GE and Mobay) manufacture polycarbonates (PC) in three plants (see Table 3). The capacity for the manufacture of PC requires an annual capacity of 92 million pounds of phosgene or about 5 percent of total U.S. phosgene capacity.

GE's entire 60 million pound capacity for phosgene is used in the manufacture of PC (Lexan®). Mobay uses about 32 million pounds of phosgene per year for polycarbonates. Mobay's total phosgene capacity is about 500 million pounds per year. In addition to PC, Mobay makes TDI, MDI, and 7 miscellaneous isocyanates.

Chemistry

Polycarbonates are made by reacting a diol (glycol) directly with phosgene. The only diol of important commercial significance is bisphenol-A. The equation is:



Bisphenol-A Phosgene PC

PC is a clear, colorless, tough plastic that competes with polymethylmethacrylate (PMMA) and specially treated glass in the shatter-resistant glazing industry.

Like TDI and MDI, PC is prepared directly from phosgene with no significant purification of the final polymer. PC, therefore, requires a very high purity phosgene in its manufacture. Surplus Army phosgene without extensive purification (redistillation) would not be suitable for PC manufacture.

Manufacturers of Monoisocyanates

Companies that manufacture monoisocyanates from captive phosgene are indicated in Table 3. Companies that produce isocyanates from either purchased or captive phosgene are listed in Table 4. Companies that use purchased phosgene to prepare monoisocyanates are naturally likely prospects for purchasing surplus Army phosgene.

Chemistry

The basic chemistry of isocyanates is outlined briefly in earlier sections on Chemistry under Manufacture of Diisocyanates and Reactions of Isocyanates.

An important fact is that the monoisocyanates are usually low olecular weight chemical species and consequently can be purified by istillation. Thus, impurities in surplus Army phosgene will usually be emoved from monoisocyanates during the conventional purification techniques. or this reason, manufacturers of monoisocyanates could probably use urplus Army phosgene without prior distillation. Solid particulate matter ould block lines, plug valves and gum up equipment, so filtration is robably desirable.

Manufacturers of Other Chemical Derivatives and Intermediates Produced from Phosgene

Table 4 also lists companies that produce other chemical ntermediates produced from phosgene. Some of these intermediates are:

- Carbonates
- Peroxycarbonates
- Chloroformates
- Chlorothioformates
- Carbamoyl chlorides.

hemistry

The following equations indicate how the above intermediates ould be produced from phosgene.

TABLE 4. U.S. PRODUCERS OF MERCHANT PHOSGENE-DERIVED CHEMICAL INTERMEDIATES

Parent Company	Division or Subsidiary	Plant Location	Derivative
Akzona	Armak Process Chemical	Bayport, TX	Di (sec-butyl) peroxydicarbonate Di (2-ethylhexyl) peroxydicarbonate Di (-n-propyl peroxycarbonate Isopropyl percarbonate
Chemetron	Chemical Products	LaPorte, TX	15 chloroformates Diethyl carbonate Dimethyl carbonate Dipropyl carbonate
Eastman Kodak	Eastman Organic Chemicals	Rochester, NY	p-Nitrophenyl isocyanate p-Tolyl isocyanate Diphenyl carbamoyl chloride Phenyl chloroformate
Jakem Industries		New Haven, CT	>100 aromatic isocyanates
Minerec			Diethyl carbonate Dimethyl carbonate Ethyl chloroformate Isobutyl chloroformate Methyl chloroformate
Mobay Chemical[(a)]	Industrial Chemicals	New Martinsville, WV	_m_-Chlorophenyl isocyanate _p_-Chlorophenyl isocyanate 3,4-Dichlorophenyl isocyanate Phenyl isocyanate Ethyl chlorothioformate

Parent Company	Division or Subsidiary	Plant Location	Derivative
Pennwalt	Lucidol	Buffalo, NY	Dicetyl peroxydicarbonate
			Dicyclohexyl peroxydicarbonate
		Genesseo, NY	*tert*-Butyl peroxyisopropyl carbonate
			Di (sec-butyl) peroxydicarbonate
			Di (n-propyl) peroxydicarbonate
PPG	Industrial Chemicals	Barberton, OH	Allyl diglycol carbonate
			tert-Butyl peroxyisopropyl carbonate
			Di (sec-butyl) peroxydicarbonate
			Di (2-ethyl hexyl) peroxydicarbonate
			Di-n-propyl peroxydicarbonate
			Isopropyl chloroformate
			Isopropyl percarbonate
R.S.A.		Ardsley, NY	Benzl chloroformate
			2-Chloroethyl carbonate
			2-Chloroethyl chloroformate
			Phenyl carbonate
			Tetra isoamylammonium thiocyanate
Stauffer		Cold Creek, AL	n-Propyl chlorothioformate

Parent Company	Division or Subsidiary	Plant Location	Derivative
Story Chemical[b]	Ott	Muskegon, MI	n-Butyl isocyanate p-Chlorophenyl isocyanate 3,4-Dichlorophenyl isocyanate Ethyl isocyanate Isopropyl isocyanate Methyl isocyanate Phenyl isocyanate Propyl isocyanate
Union Carbide	Chemicals and Plastics	Institute and South Charleston, WV	Methyl isocyanate
Upjohn	Fine Chemical	North Haven, CT	*tert*-Butyl isocyanate *p*-toluenesulfonyl isocyanate
	Polymer Chemicals	LaPorte, TX	*n*-Butyl isocyanate *tert*-Butyl isocyanate Phenyl isocyanate TODI PMPI

(a) Subsidiary of Bayer AG of West Germany.

(b) Company filed for bankruptcy in 1976. Cordova, the buyer of the plant and technology, is not manufacturing isocyanates and does not plan to do so before 1980.

Sources: (1) Industry contacts.

(2) Stanford Research Institute, 1977 Directory of Chemical Producers, Menlo Park, CA (1977).

$$ClCOCl + 2ROH \longrightarrow RO\overset{\overset{O}{\|}}{C}OR + 2HCl$$

dialkyl carbonate

$$ClCOCl + H_2O_2 + 2ROH \longrightarrow RO\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}OR + 2HCl$$

dialkylperoxycarbonate

$$ClCOCl + ROH \longrightarrow RO\text{-}\overset{\overset{O}{\|}}{C}\text{-}Cl + HCl$$

alkyl chloroformate

$$ClCOCl + R_2NH \longrightarrow R_2N\text{-}\overset{\overset{O}{\|}}{C}\text{-}Cl + HCl$$

dialkyl carbamoyl chloride

$$ClCOCl + RSH \longrightarrow RS\text{-}\overset{\overset{O}{\|}}{C}\text{-}Cl + HCl$$

alkyl chlorothioformate

Manufacturers of Pesticides Produced from Phosgene

Table 5 lists 11 companies that produce 29 pesticides whose basic aw material is phosgene. It should be noted that all of these companies o not necessarily handle phosgene. They might purchase some of the ntermediates such as chloroformates or carbamoyl chlorides discussed in the revious section.

hemistry

Phosgene has two reactive chlorines that will react sequentially ith active hydrogens attached to heteroatoms (i.e., ROH, R_2NH, RSH). The omenclature of the products is indicated in the following tabulation.

TABLE 5. U.S. MANUFACTURERS OF PESTICIDES BASED ON PHOSGENE

Company	Plant Location	Pesticide Name (Type)[a]	Raw Materials other than Phosgene	Capacity, million pounds
Ciba-Geigy	McIntosh, AL	Maloran® (Chlorobramuron) (H-U)	3-Cl-4-Br-aniline + O,N-dimethylhydroxylamine	NA
	Toms River, NJ	Tenoran® (Chloroxuron) (H-U)	p-Cl-phenoxyaniline + dimethylamine	NA
	McIntosh, AL	Fluometuron (H-U)	m-trifluoromethylaniline + dimethylamine	NA
Colorado International	Palacios, TX	Diuron (H-U)	3,4-dichloroaniline + dimethylamine	
DuPont	Belle, WV	Benonyl® (benlate) (F-C)		
	LaPorte, TX	Diuron (H-U)	3,4-dichloroaniline + dimethylamine	30[b]
		Lorox® (linuron) (H-U)	3,4-dichloroaniline + O,N-dimethylhydroxylamine	30[b]
		Tupersan® (siduron) (H-U)	aniline + 2 methylcyclohexylamine	30[b]
		Telvar (monuron) (H-U)	p-Cl-aniline + dimethylamine	30[b]
		Methomyl (I-C)	methylamine + methyl thiomethylketone oxime	5
		oxamyl (Vydate®) (I-C)	methylamine + 2-oximino-2-thiomethyl-N,N-dimethylacetamide	1
FMC	Middleport, NY	Furadan® Carbofuran (I-C)	methylamine + 2,3-dihydro-2,2-dimethyl-7-hydroxybenzofuran	15
		Tandex® (H-C)	dimethylamine + m-aminophenol + t-butyl isocyanate	NA
Gulf	Pittsburgh, KA	Carbyne® barban (H-C)	m-Cl-aniline + 4-Cl-2-butynol-1	NA
Eli Lilly	Lafayette, IN	Spike® tebuthiuron (H-U)	methyl amine + a 1,3,4-thiadiazolamine	NA

TABLE 5. (Continued)

Company	Plant Location	Pesticide Name (Type)[a]	Raw Materials other than Phosgene	Capacity, million pounds
Nor Am Ag.	Chicago, IL	Carzol® (formetanate) (I-C)	methyl amine + 3-(dimethylaminomethylene-imino) phenol	1
	Memphis, TN	Fluometuron (H-U)	m-trifluoromethylaniline + dimethylamine	NA
PPG	Barberton, OH	Propham (H-C)	aniline + isopropyl alcohol	3
		Furloe (chlorporpham) (H-C)	m-Cl-aniline + isopropyl alcohol	7
Shell	Denver, CO	Methomyl (Nudrin®) (I-C)	methylamine + methyl thiomethylketone oxime	2
	Mobile, AL	Aldicarb (I-C)		
Stauffer	Cold Creek, AL St. Gabriel, LA	Eptam® (EPTC)[c] (H-T)	ethyl mercaptan + di-n-propylamine	NA
	Cold Creek, AL	Ordram® (molinate) H-T)	ethyl mercaptan + hexamethyleneimine	NA
		Ro-Neet® (cycloate) (H-T)	ethyl mercaptan + N-ethyl cyclohexylamine	NA
		Sutan+® (butylate) (H-T)	ethyl mercaptan + diisobutylamine	NA
		Tillam® (pebulate) (H-T)	n-propyl mercaptan + n-butyl ethylamine	NA
		Vernam® (vernolate) H-T)	n-propyl mercaptan + di-n-propylamine	NA
Union Carbide	South Charleston, WV	Sevin® (Carbaryl) (I-C)	methyl amine + 1-naphthol	100
		Temik® (aldicarb) (I-C)	methyl amine + 2-methyl-2-thiomethyl-N,N-dimethylacetamide	4

(a) H = herbicide, I= insecticide, F = fungicide, U = urea, C = carbamate, T = thiocarbamate

(b) DuPont's capacity is for all urea herbicides.

(c) Also made at St. Gabriel, LA.

Starting Materials		Products	
Reactant 1	Reactant 2	Structure	Class Name
ROH	-	ROCOCl	chloroformate
ROH	R'OH	ROCOOR'	carbonate
ROH	$R'NH_2$	ROCONHR'	carbamate or urethane
RNH_2	-	RNCO	isocyanate
RNH_2	$R'NH_2$	RNHCONHR'	urea
R_2NH	-	R_2NCOCl	carbamoyl chloride
R_2NH	R'_2NH	$R_2NCONR'_2$	urea
RSH	-	RSCOCl	chlorothioformate
RSH	R'SH	RSCOSR'	dithiocarbonate
RSH	R'OH	RSCOOR'	thiocarbonate
RSH	$R'NH_2$	RSCONHR'	thiocarbamate

APPENDIX A

COMPANIES CONTACTED

TABLE A-1. COMPANIES CONTACTED

Company	Degree of Interest Phosgene	Degree of Interest Cylinders	Comments
Allied	N	N	Require 99.9%. Purify by Zn filings
BASF Wyandotte	M	N	Fe a problem
Rubicon	M	N	Obtained phosgene free from Mr. Gershon
Chemetron	L	L	CCL_4 a problem, condition of valves?
Dow	N	N	Cl_2 worst contaminant. Add CO and pass over C bed
DuPont	N	N	
FMC	N	N	Discontinued phosgene production in 1974
GE	N	N	No interest
Texaco (Jefferson)	N	N	No longer producing phosgene or MDI
Minerec	M	N	Would bid jointly with Delta who wants cylinders
Mobay	N	N	Cl_2 is bad, require 99.9% phosgene
Olin	M	N	Prohibitive cost for redistillation
PPG	N	N	
Stauffer	N	N	Require 99 + % phosgene
Story (Cordova)	N	N	No current interest by Cordova
Union Carbide	L	N	Free chlorine is disastrous for TDI
Upjohn	N	N	Require very high purity for pharmaceuticals
Van de Mark	N	N	
Akzona	N	N	Purchase chloroformates from Chemetron
Eastman Kodak	L	N	Purchase small amounts from Chemetron and Van de Mark
Jakem Indust.	N	N	Uses 100-pound cyliners

Company	Degree of Interest Phosgene	Degree of Interest Cylinders	Comments
Pennwalt	N	N	Peroxydicarbonates require high purity phosgene
RSA	N	N	
Ciba Geigy	N	N	C-G discontinued phosgene route 10 years ago
Consolidated Chem.	H	H	They now use 9 cylinders/day
Gulf	N	N	They buy isocyanate from Mobay
Eli Lilly	N	N	They use less than 100 lbs./year
Nor Am Ag.	N	N	They buy ready-made pesticides
Shell	N	N	Pesticides and intermediates are made by Union Carbide
Chem. Commodities	H	H	Now have guaranteed customer for phosgene
Delta Chem	L	M	
Jones Chemical	M	H	Will sell the phosgene
Matheson Gas Products	M	N	
Scientific Gas Products	N	N	
Air Products & Chem	N	N	
Worthington Steel	N	N	Produce low pressure cylinders only
Manley-Regan	N	H	Interest in storage cylinders for chlorine
Harsco Corp.	N	N	Small cylinders only
Columbiana Boiler	N	N	Scrap value of cylinders = $45
Union Carbide-Linde	L	H	

Source: Battelle interviews.